

A generalized Mittag-Leffler function to describe nonexponential chemical effects

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Abstract

In this paper a differential equation with noninteger order was used to model an anomalous luminescence decay process. Although this process is in principle an exponential decaying process, recent data indicates that is not the case for longer observation time. The theoretical fractional differential calculus applied in the present work was able to describe this process at short and long time, explaining, in a single equation, both exponential and non-exponential decay process. The exact solution found by fractional model is given by an infinite serie, the Mittag-Leffer function, with two adjusting parameters. To further illustrate this nonexponential behaviour and the fractional calculus framework, an stochastic analysis is also proposed.

Keywords: Luminescence emission · Nonexponential decay · Fractional calculus · Monte Carlo method

1 Introduction

The question about validation of radioactive decay law has a long history and two reasons for this can be considered. One is that accurate experimental data at very long time are difficult to obtain. For example, for the α -decay of ^8Be the deviation from exponential decay is expected after 30 half lives, when the signal intensity becomes of order 10^{-7} of the initial intensity [1]. The other reason is that the exponential decay law can be derived only as an approximate result of quantum mechanics theory. A rigorous quantum study shows that at very short and very long time unstable state decays with nonexponential dependence of time [2, 3].

Until recently the experimental searches for nonexponential behavior was mainly focused on nuclear decay [4–6], in which, as discussed, the experimental measurements are difficult to perform accurately in such a long time. If nonexponential decay is confirmed for nuclear decay, this deviation will affect the radiocarbon dating, as suggested by Aston [7, 8]. Experimental effort has now been directed to the study of luminescence decays of some organic materials after pulsed laser excitation [9, 10] and in this case the intensity data can be obtained with relatively less difficulty if compared with nuclear radiation decay. The first experimental confirmation of the nonexponential decay law, using luminescence data, was presented by Rothe and coworkers, in 2006 [10]. These authors observed that, as expected, initially luminescence decays obeys the radioactive decay law, but after some half lives the fluorescence decays significantly slower, turning into a different decaying law. In the study by Rothe and coworkers the experimental data were fitted to two different functions: an exponential function up to about 0.6ns, and after which it was used a power function.

This problem can be analysed in different way by using fractional calculus. Recent studies have shown that fractional calculus is a good alternative mathematical tool into many fields of science, such as the study of the growth of bacteria in culture media [11], the mechanisms by which diseases spread [12] and the kinetics of drug absorption [13]. The use the fractional calculus was explored in nuclear decay by Çalik[14], in which a comparison between experimental data and theoretical model was made with just one half lives and always at short time when exponential behavior dominates.

In the present work a differential equation with fractional order will be presented as an attempt to generalize the model to exponential and nonexponential luminescence decay of polyfluorene. For the first time, experimental data for luminescence decays, at short and long time, will be compared with the proposed model indicating that fractional model is adequate to describe exponential and nonexponential chemical luminescence decay process. Another issue to be considered here is how to define the probability in this luminescence decay process when described by fractional differential equation. In a comparison with models of integer orders, probability of dN particles undergoing emission will here be defined using the Mittag-Leffer function.

2 Fractional calculus background

Fractional calculus has its roots in a discussion between Leibniz and L'Hospital about the meaning of $d^{1/2}f(x)/dx^{1/2}$ as described in a book on the subject [15]. Nowadays, fractional calculus is a branch of mathematics analysis

that generalizes the derivative and integral with noninteger order.

Theoretical description of fractional calculus may start by integrating $(Jf)(t) = \int_0^t f(s)ds$ with respect to s by $m = (n - l)$ times from which one obtains [16],

$$(J^{(n-l)}f)(t) = \frac{1}{\Gamma(n-l)} \int_0^t (t-s)^{n-l-1} f(s) ds \quad (1)$$

with Γ the gamma function. On the other hand, the differential operator, D , can be further applied n times to this integral to furnish,

$$(D^n J^{n-l}f)(t) = (D^l f)(t) \quad (2)$$

Therefore, for a non-integer number $l = \alpha$, one obtains Riemann-Liouville fractional derivative. Another attempt to define was made by Caputo, [16] as

$$(D^\alpha f)(t) = (J^{n-\alpha} D^n)f(t) = \frac{1}{\Gamma(n-\alpha)} \int_0^t \frac{f^{(n)}(s) ds}{(t-s)^{\alpha-n+1}} \quad (3)$$

in which $n \leq \alpha \leq n+1$, $\alpha \in \mathcal{R}$, $n \in \mathcal{N}$ and $f^{(n)}(s) = d^n f/ds^n$. In this case α is interpreted as the fractional derivative order. Equation (3) is known as Caputo fractional derivative of order α , that is in fact an Abel integral equation [18]. Dealing with fractional derivative and inverting Abel integral equation, an ill-posed problem, are equivalent problems.

The Caputo fractional derivative is a nonlocal operator for it depends on the strain history from 0 to t . This should be contrasted with a derivative of integer order, a clear local operator. Consequently the fractional derivative in time contains information about the function at earlier points, an effect known as memory effect which will be explored along the current work. This definition of fractional derivative can be used to model the rate change because derivative of a constant is zero, unlike Riemann-Liouville definition. Therefore, henceforth make the assumption that $D^\alpha f(t)$ is Caputo fractional derivative.

3 A generalized decay law

An unimolecular process is described by

$$dN(t)/dt = -kN(t), \quad (4)$$

with the solution given by $N(t) = N(0)e^{-kt}$. The constant k is the decay constant, $N(t)$ the number of species present at a time t and $N(0)$ is the number of particles at initial time. This is an example of a process described by an integer order derivative. Although the unimolecular model is the one normally used to describe the emission intensity $I(t) = N(t)/N(0)$ of a luminescence process, recent experimental data evidence that can not be the case for long observation time.

As luminescence decays behavior changes with time, it we will assume that the memory effect have an important role in decays process. One way to include this effect is to use fractional derivative order in the model. Investigation of the chemical luminescence process by a fractional derivative order has to start by the Caputo derivative,

$$D^\alpha I(t) = -\lambda I(t) \quad (5)$$

and, as to be discussed, will correct to describe luminescence experimental data in both regions: exponential and nonexponential part. This is the first study in the literature of such a data using fractional analysis. If fraction order is equal a one recovers the usual description of this process, equation (4). Henceforth we will assume that $N(0) = 1$ and $N(t) = I(t)$.

Laplace transformation and fractional derivative

Consider the initial value problem (5), with $n - 1 < \alpha \leq n$ and initial conditions given by $[D^l N(t)]_{t=0} = b_l$ where $l = 1, 2, \dots, n$. Applying Laplace transform to both sides of the differential equation (5), that is $\mathcal{L}[(D^\alpha N)(t)] = \mathcal{L}[-\lambda N(t)]$, using the property [16, 17]

$$\mathcal{L}[(D^\alpha N)(t)] = s^\alpha \mathcal{L}[N(t)] - \sum_{k=0}^{n-1} s^{\alpha-k-1} [D^k N(t)]_{t=0} \quad (6)$$

and after some simple algebraic manipulation, one obtains

$$\mathcal{L}[N(t)] = \sum_{l=1}^n \frac{b_l s^{\alpha-l}}{s^\alpha + \lambda} \quad (7)$$

where $l = k + 1$ and $b_l = [D^l N(t)]_{t=0}$. The function that satisfies each term of Equation (7) is the Mittag-Leffer function with two parameter, $E_{\alpha,\beta}(-\lambda t^\alpha)$, such which [16, 17]

$$\mathcal{L}[t^{\beta-1} E_{\alpha,\beta}(-\lambda t^\alpha)] = \frac{s^{\alpha-\beta}}{s^\alpha + \lambda}, \quad (8)$$

Therefore, solution of Equation (5) is given by

$$N(t) = \sum_{l=1}^n b_l t^{l-1} E_{\alpha,l}(-\lambda t^\alpha) \quad (9)$$

If consider α between 0 and 1, and initial condition $b_1 = 1$, one obtains

$$N(t) = E_{\alpha,\beta}(-\lambda t^\alpha) \quad (10)$$

Equation (10) represents a generalized decay law for the present study and which will be used to describe experimental data of luminescence intensity emission of a organic molecule, after pulsed laser irradiation. The quantities, α and β are considered as parameters that have to be estimated. Equation (10) was previously used to study of pharmacokinetics [13] and nuclear decay [14] with $\beta = 1$. The proposed model reproduces purely exponential behavior when $\alpha = \beta = 1$.

Mittag-Leffer function with two parameter

The Mittag-Leffer function with two parameter can be seen as a generalization of the exponential function defined by the following infinite power series [19]

$$E_{\alpha,\beta}(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(\alpha k + \beta)} \quad (11)$$

with $\alpha, \beta > 0$, in which $E_{\alpha,\beta}(x) = e^x$ when $\alpha = \beta = 1$. This function have interesting asymptotic properties, which was studied by Mainardi [19]. In his work he showed that for $t \rightarrow 0$ Mittag-Leffer function with two parameters converges to exponential function whereas to $t \rightarrow \infty$ converges to $1/t^{\alpha r}$, therefore

$$E_{\alpha,\beta}(-t^\alpha) \approx \begin{cases} \exp\left[-\frac{t^\alpha}{\Gamma(\beta+\alpha)}\right], t \rightarrow 0 \\ \sum_{r=1}^{\infty} (-1)^{r-1} \frac{t^{-\alpha r}}{\Gamma(\beta-\alpha r)}, t \rightarrow \infty \end{cases} \quad (12)$$

As these asymptotic behavior is similar to that observed in the Rothe experimental data, motivated us to study the fractional calculus in luminescence decay of polyfluorene.

Monte Carlo Method

The Monte Carlo method [20] is employed to simulate the luminescence decays of organic substance after pulsed laser excitation. The probability of emission, $P = dN/N$, can be obtained by differentiating Equation (10) with respect to t ,

$$dN = -\lambda \alpha t^{\alpha-1} dt \frac{dE_{\alpha,\beta}(x)}{dx} \quad (13)$$

in which [16, 17]

$$\frac{dE_{\alpha,\beta}(x)}{dx} = \frac{E_{\alpha,\beta-1}(x) - (\beta-1)E_{\alpha,\beta}(x)}{\alpha x} \quad (14)$$

and $x = -\lambda t^\alpha$. Under this considerations, the probability P can be found, such as

$$\frac{dN}{N} = t^{-1} dt \left[\frac{E_{\alpha,\beta-1}(-\lambda t^\alpha)}{E_{\alpha,\beta}(-\lambda t^\alpha)} - (\beta-1) \right] \quad (15)$$

and simulation can be carried out by Monte Carlo approach. The proposed equation reproduces the exponential behavior when $\alpha = 1$ and $\beta = 1$, for in this case $P = \lambda dt$ whereas $E_{1,0}(-\lambda t) = -\lambda t E_{1,1}(-\lambda t)$. The result obtained by Monte Carlo method will be compared with those obtained from Equation (10).

4 Results and discussions

Fractional calculus modelling

Rothe and coworkers studied luminescence decays of polyfluorene after pulsed laser excitation for a time enough to observe nonexponential behavior [10]. Figure 1 shows their experimental results together with two

adjustments to the experimental data: one of them for the exponential decay region and the other for nonexponential one. Nonexponential behaviour presents a decay law as a power law, in which emission intensity at time t is proportional to t^{-n} . For polyfluorene Rothe and coworkers determined $n = 2.1$, by a linear adjustment of $(\ln N(t) \times \ln(t))$, at long time.

The time in which a change in the decay behavior occurs can be defined by intersection of exponential law and power law, as shown in Figure 1. For polyfluorene substance this times was determined to be about 2.7 ns from the initial time, or about 11 half lives after ($t_{1/2}=0.25$ ns). In the study by Çalik[14] on nuclear decay, the fractional order was found using only radiation intensity at one half life, and in this case it was found fractional order smaller than 1. Previous result can not explain the behavior of nuclear decay curve off half life. Here, the whole decay curve, with experimental data at short and long time, was fitted by fractional calculus and not just one single experimental data such as radiation intensity at half life.

The code developed by Podlubny [21] was used in this paper to determine the Mittag-Leffler function. Initially the behaviour of luminescence decay is exponential, therefore it is expected that α value is close to 1. As observed by the asymptotic series (12), the choice of α and β parameters determines the relative weight of each of the infinite series. For example, if $\alpha = \beta$ the first term of the series is zero, thus the second term takes on a more important role, whereas the other terms tend to zero faster. Therefore $E_{\alpha,\alpha}(-t^\alpha) \propto t^{-2\alpha}$ when $t \rightarrow \infty$, and finally $n \approx 2\alpha$. By previous supposition $\alpha \approx 1$ and ,therefore, $n \approx 2$ which is the case for polyfluorene. These values of α and β were used as initial choice.

In figure 1 continuum line represents the interpolation by equation (10), which was obtained with a value of $\alpha = \beta = 0.999$ and $\lambda = 2.8 \times 10^9 \text{ ns}^{-1}$. The model parameters, α , β and λ , were determined using Simplex method [20] with the objective function defined by sum of squared difference between experimental and calculated values. As can be seen, the Mittag-Leffer function with two parameters reproduce experimental data with good agreement at short and long time. In other words, with Equation (10) it was possible to reproduce, using only one function, the two different behavior: exponential and nonexponential. The goodness of fit can be evaluated by the relative error between experimental data and predict results, which is less than 1.5%. Calculated data by fractional model were adjusted by two linear equation, at short $(\ln N(t) \times t)$ and long $(\ln N(t) \times \ln t)$ time. The parameter $\tau = 1/\lambda = 0.36$ ns and $n = 2.1$ also are in excellent agreement with those obtained using experimental data: $\tau = 0.35$ ns and $n = 2.3$. In figure 1, the dashed line represents the result obtained from equation (4).

Monte Carlo simulation

The Monte Carlo method was further used to simulate and elucidate luminescence decays when described by differential equation with fractional order. In this simulation to radioactive decay the probability that a element undergoes changes in time t is given by Equation (15).

The simulation was performed with $N=50\,000\,000$ and Mittag-Leffer function was calculated by Podlubny routine[21] with accuracy of 10^{-12} . Figure 2 shows the intensity decay as function of time obtained by Monte

Carlo method together with the results obtained by equation 10. The relative error observed was less than 0.7 %. Therefore, one may conclude that the probability defined by Equation (13) is adequate to describe luminescence decays at wide range of time.

For differential equation with integer order the probability as function of time is constant during all process. On the other hand, when noninteger order is used the probability changes with time. Therefore, when considering derivatives with noninteger order, the probability that dN particles undergo emission not only depend of number of particle at time t, but on the whole process. The reason for this is that fractional derivative is defined by integral equation as shown previously. This effect is well known in other problems with fractional derivative and named as memory effect [11–13].

5 Conclusions

The solution found by fractional model was given by Mittag-Leffler function with two parameters, which was able to interpolate experimental data between 1 ns and 100 ns, unlike previous studies in which few data at short time were used. For polyfluorene molecule this interval is so long that it was possible to observe a change in the exponential behavior. Our model with fractional order coincide with experimental data within a relative error less than 1.5%. The parameters used in Mittag-Leffler function fit were $\alpha = \beta = 0.999$ and $\lambda = 0.36$.

The probability of dN particles undergoing emission was here defined for the first time using Mittag-Leffler function with two parameters, and the Monte Carlo method was employed to simulate the luminescence decays of polyfluorene molecule. A good agreement between exact result and Monte Carlo approach was also obtained, with a relative error less than 0.7%. This result shows that our definition of probability is adequate to describe experimental data in a wide range of time, taking into account memory effect, by using noninteger order in differential equation.

Acknowledgments

We would like to thank CNPq and FAPEMIG for their financial support.

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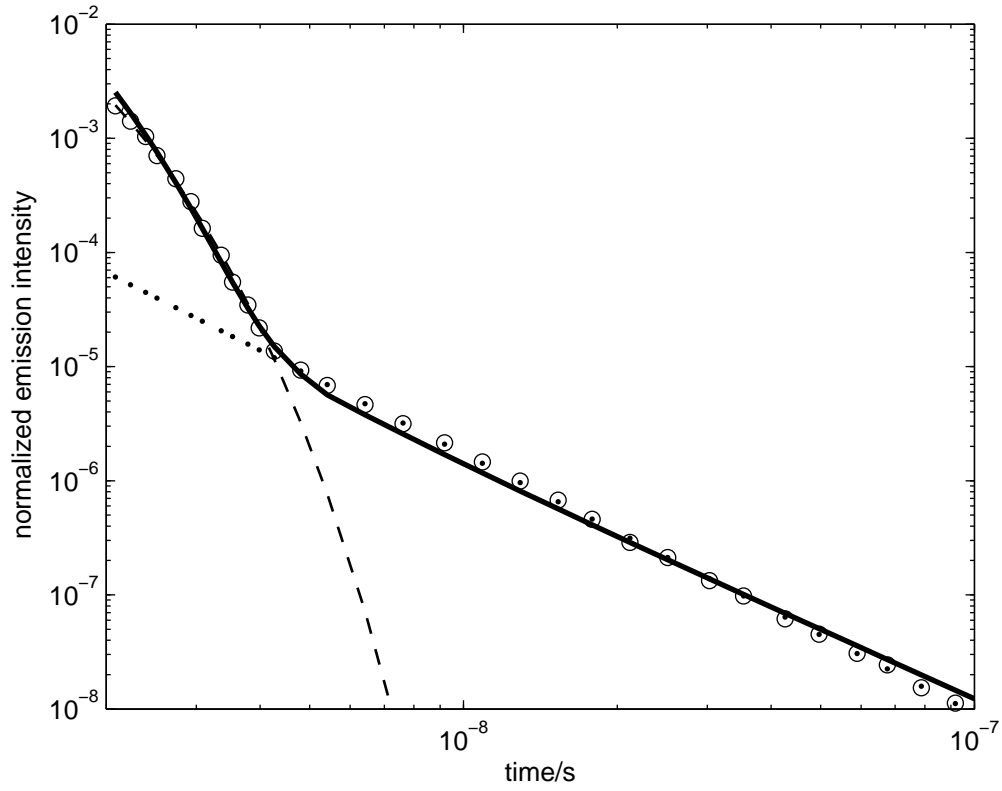


Figure 1: Experimental data for luminescence decay as open circle symbols, taken from the Rothe's work [10]. Exponential and power law are indicated by dashed and dotted line, respectively. The continuous line represents the result obtained by the present work.

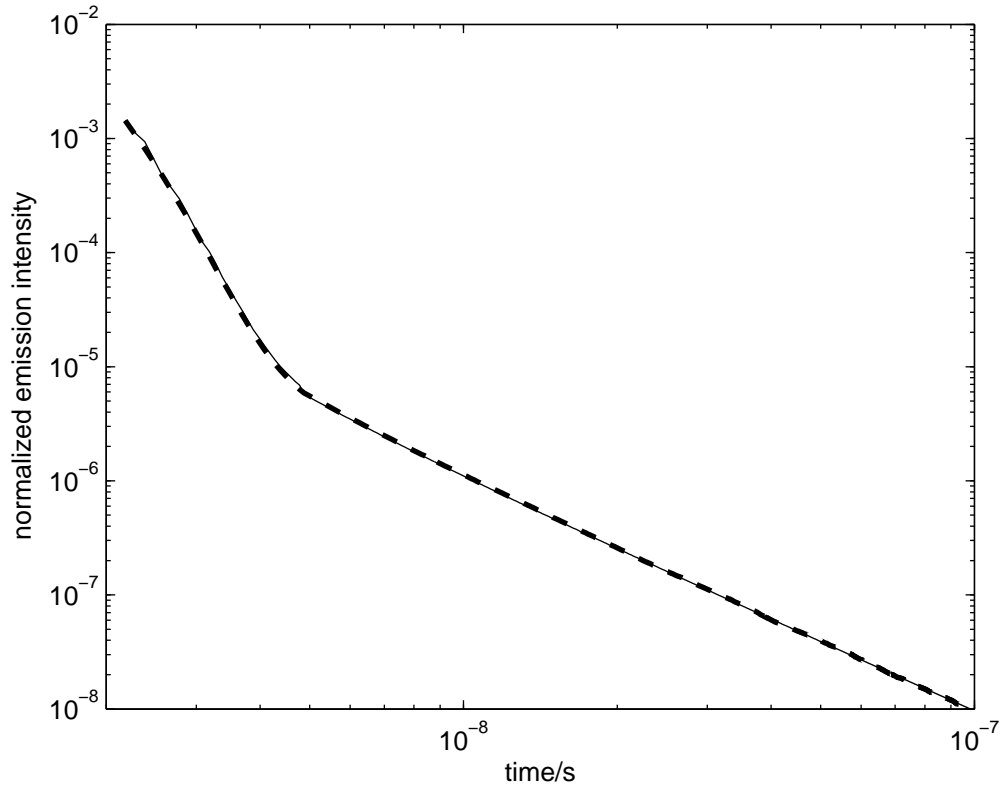


Figure 2: Present theoretical result (continuous line), together with result obtained by Monte Carlo method (dashed line).